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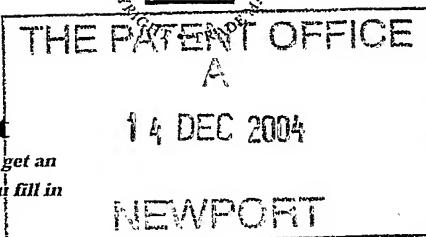
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Description 13

Claim(s) *CF*

Abstract

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### STEAM ELECTROLYSIS

The present invention relates to hydrogen production, and more particularly to hydrogen production by high temperature steam electrolysis with improved efficiency and reduced cost.

5

Hydrogen is becoming an increasingly important fuel. Various processes have been developed for producing it including inter alia, steam reforming of natural gas and by coal gasification, and water electrolysis. Existing processes do, however, suffer 10 from various disadvantages including relatively low efficiency and high production costs.

It is an object of the present invention to avoid or minimize one or more of the above-mentioned disadvantages.

15

It has now been found that by using a proton conducting electrolyte membrane, which is substantially non-permeable to oxide ions and to molecular gas, and is stable at high temperatures, it is possible to dissociate water into hydrogen 20 and oxygen and at the same time separate the hydrogen from the oxygen.

Thus in one aspect the present invention provides a method of producing hydrogen comprising: providing a steam feed stream, 25 contacting said steam feed stream with a proton conducting membrane supported on a porous redox stable substrate, through said substrate, said membrane being substantially non-permeable to molecular gas and to oxide ions, applying a DC voltage across an anode coupled to the substrate side of said membrane and a 30 cathode coupled to the other side of said membrane so as to dissociate at least part of said feed stream therebetween, into protonic hydrogen and oxygen at said anode, allowing said

protonic hydrogen to pass through said membrane and form molecular hydrogen at said cathode, and collecting said molecular hydrogen.

- 5 In another aspect the present invention provides a steam electrolyser for producing hydrogen, comprising: a dense proton-conducting membrane substantially non-porous to molecular gas, said membrane being supported on a gas permeable, chemically and mechanically stable, electronically conducting substrate, said
- 10 membrane being coupled: at the substrate - supported side to an anode for connection to a positive voltage, and to a steam inlet and oxygen outlet for feeding a steam feed stream into said substrate and exhausting oxygen gas released therefrom; and at its other side to a cathode for connection to a negative voltage
- 15 and a hydrogen gas outlet for exhaustion of hydrogen gas released at said cathode.

It should be noted that in the simplest case the anode may simply form part of the substrate adjoining the membrane where a suitable substrate is employed i.e. where the substrate material is electrochemically active. Alternatively the anode may comprise a thin layer of a different material interposed between the membrane and the substrate support.

- 25 With the present invention the hydrogen production process is substantially simplified, whilst having a relatively high efficiency, and uses apparatus of relatively economic construction. The process provides hydrogen gas which is free from oxygen, steam and other gases, thereby avoiding the need
- 30 for any downstream separation of gases. Also the electrolysis

and separation out of hydrogen gas, may be achieved without the need for any expensive precious metal catalysts or the like.

Various proton-conducting materials are known in the art which  
5 are stable to a greater or lesser extent at high temperatures.  
In general steam electrolysis is carried out at temperatures of  
around 900 to 1000 °C. A particular advantage of the present  
invention is, however, that steam electrolysis can be carried  
out at significantly lower temperatures, for example, from 500  
10 to 700 °C, whereby the materials and construction used may be  
significantly simplified and reduced in cost. In general  
suitable proton-conducting materials comprise a material which  
allows the reversible dissociation of water into its lattice to  
form mobile protonic carriers therein. Such materials are  
15 frequently oxygen deficient perovskites of formula  $\text{ABO}_{3-\delta}$ .

Particular preferred materials which may be mentioned include  
 $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  (BCY10),  $\text{Sr}_3\text{CaZr}_{0.5}\text{Ta}_{1.5}\text{O}_{8.75}$  (SCZTO) and  
 $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{8.73}$  (BCN18),  $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  (BZY) as well as composites  
20 of such materials. Thus, for example, there may be used a  
membrane comprising a layer of BCY10 which has relatively high  
electrochemical performance (in terms of proton conduction) in  
contact with the substrate, with an outer protective layer of  
SCZTO which has better stability - especially against chemical  
25 degradation by atmosphere  $\text{CO}_2$ .

As indicated above, it is also important that the membrane  
should be substantially impermeable to molecular gas.  
Accordingly the membrane material needs to be in a substantially  
30 dense, non-porous, form. The membrane is also substantially  
impermeable to oxide ions.

In order to maximize the efficiency of the electrolyser, the resistivity of the membrane should be kept as low as possible. Desirably therefore the membrane should be as thin as is reasonably practicable. Preferably the membrane thickness is

5 not more than 25  $\mu\text{m}$ , advantageously from 1 to 25  $\mu\text{m}$ , most preferably from 3 to 15  $\mu\text{m}$ .

It is also important that the membrane should remain stably attached to the substrate support under the high temperature

10 operating conditions of the electrolyser. Various methods are known in the art for forming thin-films on substrates including inter alia: sol-gel techniques in which a liquid suspension is applied to a substrate, dried and then cured; tape casting in which the membrane material is provided in a powder form

15 embedded inside a polymer tape which is placed on the surface of the substrate and heat treated to form a substantially continuous film of membrane material; vacuum deposition in which the membrane material is provided in a powder form suspended in a liquid carrier is placed on the surface of the substrate and

20 drawn into the surface thereof by means of a vacuum applied to the remote side of the porous substrate, and then heat treated to form a substantially continuous film of membrane material at the substrate surface; etc. It will be appreciated in relation to such processes that, in accordance with normal practice, the

25 particle size of the membrane material applied to the surface of the porous substrate should not be significantly less than the pore size of the substrate, in order to minimize penetration of the particles into the interior of the substrate. Using such techniques we have successfully obtained proton conducting

30 ( $\text{Sr}_3\text{CaZr}_{0.5}\text{Ta}_{1.5}\text{O}_{8.75}$ ) membrane films on porous conductive substrates (NiO:YSZ and LSM) with film thicknesses in the range

from 3 to 100 microns, depending on the number of layers deposited.

Membranes of BaZrO<sub>3</sub>-based materials are especially preferred as these are stable and exhibit high proton conductivity. Those materials have, though, to be sintered at a temperature above 1600°C which makes it very difficult to find suitable electrode materials which have so high a melting point without undergoing significant chemical reactions with the BaZrO<sub>3</sub>-based electrolyte. By using a sintering aid such as ZnO, it is, however, possible to reduce substantially the sintering temperature, whilst still obtaining a high density product and substantially maintaining the desirable properties of high proton conductivity and stability. More particularly we have found that by using a relatively small amount of ZnO - typically around 1% w/w, it is possible to reduce the sintering temperature of BaZr<sub>2</sub>Y<sub>2</sub>O<sub>9</sub> from around 1700°C to around 1300°C, and obtain a high density material with a relative density of the order of 96%.

20

In general suitable sintering aids comprise Al<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> and some first row transition elements oxides such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CoO, CuO etc, which are commonly used as sintering aids for obtaining dense ionic conducting materials such as yttria stabilised zirconia (YSZ) and ceria doped with gadolinia (CGO).

In order to have a significant effect in reducing the sintering temperature, it is generally necessary to use a minimum amount of the sintering aid. This can be readily determined by trial and error and is typically of the order of from 0.1 to 0.5 %w/w. In order to avoid significant distortion of the membrane

material structure and adverse effects on the proton-conducting and stability properties thereof, it is generally desirable that the amount of sintering aid should be minimized - whilst still maintaining a useful sintering temperature reduction. Desirably 5 there should be used not more than 5 %w/w, preferably not more than 2 %w/w, of sintering aid.

The sintering mechanism is typically due to the formation of low melting phases between the sintering aid and constituent oxides, 10 which lower the sintering temperature. Alternatively the sintering aid enters the oxide lattice and produces a lower melting phase that sinters more readily. In either mechanism the sintering aid may be lost on sintering. It will be appreciated that some sintering aids are more effective than 15 others and that some sintering aids will require higher concentrations thereof. In this connection low melting glasses such as Zn-B-O glass or Zn doped oxides are particularly good low temperature sintering aids. More particularly there may be used BO, ZnO, and mixtures thereof. Preferably though there is 20 used substantially pure ZnO.

The use of such sintering aids is similarly beneficial with other membrane material such as Barium Yttrium Cerate and especially Barium Yttrium Cerate Zirconate which combines 25 stability and conductivity performance.

Various porous electrically conducting materials which are stable at the elevated temperatures used in steam electrolyzers are already known in the art, and may be used for the substrate 30 support in the present invention. Suitable materials generally comprise a metallised ceramic or a mixed conductive oxide having

an electrical conductivity of not less than  $10 \text{ Scm}^{-1}$ , preferably not less than  $100 \text{ Scm}^{-1}$ , at the operating temperature of the steam electrolysis. Particular suitable substrate materials which may be mentioned include metallised ceramics such as 5  $\text{Cu:Al}_2\text{O}_3$  or mixed conductive oxides such as  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (LSM), chromium-doped LSM (i.e.  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ ) or  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (LSCF).

As indicated above, the substrate support requires generally to 10 be sufficiently porous to facilitate penetration of the steam molecules to the membrane and to facilitate exhaustion of oxygen molecules exiting from the membrane. In general therefore the pore size should be not less than  $0.5 \mu\text{m}$ , and conveniently from 0.5 to  $10 \mu\text{m}$ . Desirably the porosity is from 30 to 60 %, 15 preferably from 40 to 50%. Where such a discrete anode is provided between the membrane and the substrate, it will be appreciated that in such cases the membrane is supported indirectly by the substrate. Generally in such cases the anode layer is deposited on the substrate, and then the membrane layer 20 deposited onto the anode layer. Various techniques are known in the art, including those described elsewhere herein, for producing thin film layers onto substrates of various kinds.

As noted above, a thin layer (generally 10 to  $100 \mu\text{m}$ , preferably 25 30 to  $50 \mu\text{m}$ ) of the substrate support itself may conveniently function as the anode of the electrolytic apparatus, (where the substrate material is electrochemically active), and is connected to the voltage supply via a porous metal current collector in generally known manner. A porous cathode requires 30 generally to be sufficiently porous to facilitate exit of hydrogen molecules from the membrane. In general therefore the

pore size should be not less than 0.5  $\mu\text{m}$ , and conveniently from 0.5 to 10  $\mu\text{m}$ . Desirably the porosity is from 30 to 60 %, preferably from 40 to 50%. The cathode may be provided on the surface of the membrane electrolyte by painting, screen printing 5 or sol-gel coating, and is connected to the voltage supply via a porous metal current collector in generally known manner. Suitable cathodes are conveniently of a transition metal such as porous metallic platinum or palladium, or a Ni cermet of a transition metal and a proton conducting electrolyte. Various 10 mixed conducting oxides which may also be used, are known in the art including perovskite oxide materials such as those disclosed in WO2004/013925.

One of the benefits of the invention is that the lower working 15 temperatures allow the use of less expensive current collector metals such as steel, which may, if desired, be provided with electrically conducting protective film coatings, e.g. of chromium.

(as well as avoiding the use of expensive precious metal 20 catalysts etc).

The substrate supported membrane, electrode, and current collector, assembly may be electrically insulated from the gas supply and exhaust pipes and any external housing, which are 25 generally made of metal e.g. steel, by means of a high temperature glass ceramic such as barium silicate or a high temperature cement.

As indicated above the steam electrolysis may be carried out at 30 a range of different temperatures. It will also be understood that higher temperatures have the advantage of reducing the

direct electrical energy input required. It is, however, a key feature of the present invention that it allows the use of lower temperatures than have been used heretofore in steam electrolysis, which in turn allows the use of significantly more 5 economic materials and forms of construction. It is also important to avoid using higher temperatures as these can result in oxide ion conductivity developing in the membrane and even permeability to water molecules. Preferably there is used an operating temperature of from 400 to 800 °C, most preferably 10 from 500 to 700 °C.

In general it is convenient to use a steam supply at a temperature substantially equal to the desired operating temperature at the membrane. It is also possible though to 15 supply steam at a lower temperature and to heat the substrate supported membrane, e.g. using an external electrical or fuel gas (conveniently hydrogen), furnace.

It will also be understood that the voltage required to be 20 applied across the membrane for a given hydrogen flux will depend on the electrical resistance of the membrane, and any supporting substrate employed. The electrical resistance will in turn depend on the particular materials used, as well as the thickness thereof, and the operating temperature used. It is 25 accordingly desirable that the membrane should be as thin as is reasonably practicable i.e. whilst still maintaining gas tightness and structural integrity under the operating conditions used. Typically we have found that useful levels/rates of electrolysis may be obtained with an applied 30 voltage of the order of 1.1 to 1.2 V when using a proton

conducting ( $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ ,  $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{8.73}$ , etc) membrane having a thickness of around 25  $\mu\text{m}$ .

The feed stream may be supplied to the electrolysis apparatus at 5 ambient pressure. Steam generators, though, generally provide steam at super-atmospheric pressures and the use of such higher pressures - typically up to 10 bar or even 100 bar - has the advantage of increasing efficiency.

10 The steam feed stream is generally supplied to the module via piping connected to the module so that the feed stream is passed across the surface of the substrate and undissociated steam together with oxygen produced are then carried away. At the cathode side, hydrogen gas produced is also generally exhausted 15 by suitable piping. The piping (and conveniently also any external support such as a manifold or housing, for the substrate-supported membrane) may be made of any material known in the art but may conveniently be of steel or alumina, or the like.

20 The steam feed stream is generally contacted with the substrate support, by passing a flow thereof across the exposed surface thereof.

25 Further preferred features and advantages of the present invention will appear from the following detailed description given by way of example of some preferred embodiments described with reference to the accompanying drawings in which:  
Fig.1 is a schematic section through a steam electrolyser module 30 of the invention; and

Fig.2 is a schematic perspective view of a manifold interconnector for a multi-module electrolyser.

Fig.1 shows a steam electrolyser module 1 of the invention mounted in a manifold 2 and coupled to gas flow pipes 3,4 at cathode and anode sides 5,6 thereof, respectively. In more detail, the module 1 comprises a 5  $\mu\text{m}$  thick dense non-porous proton-conducting membrane 7 of BCY10 or BCN18 deposited on a 2 mm thick LSM substrate 8 having a 40% porosity and a pore size generally in the range of from 0.5 to 5  $\mu\text{m}$ .

On the outer face 9 of the membrane 7 (remote from the substrate support 8) is provided a porous metallic platinum cathode or hydrogen electrode 10, on top of which is provided a steel mesh current collector 11 connected 12 to the negative pole 13 of a DC voltage supply 14. At the anode side outer face 6 of the substrate 8 is provided a steel mesh current collector 15 connected 16 to the positive pole 17 of the DC voltage supply 14 so that a positive voltage is applied to a thin (30  $\mu\text{m}$  thick) layer 18 of the substrate 8 adjacent the membrane 7, which functions as an anode or steam electrode. The module 1 is electrically insulated from the steel manifold 2 and pipes 3,4 by a high temperature barium silicate glass ceramic seal 19.

The anode side pipe 4 has an inlet branch 4a through which high temperature steam 20 is fed in and passed across the exposed anode side outer face 6 of the substrate 8. Any undissociated steam 21, together with oxygen 22 produced by the electrolytic dissociation of the steam feed, are exhausted by an outlet branch 4b of the anode side pipe 4. The cathode side

pipe 3 is used to exhaust hydrogen gas 23 liberated at the cathode 10.

In use of the above module the following processes occur:

- 5 at the anode  $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$   
at the cathode  $4\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2$

Fig. 2 shows part of a large scale steam electrolyser comprising a manifold interconnector 24 mounting multiple modules 1 such as 10 those of Fig. 1.

**Example 1 - Preparation of Proton Conducting Membrane Material**

A nominal  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  powder was prepared by a solid state reaction method. Appropriate amounts of  $\text{BaCO}_3$ ,  $\text{ZrO}_2$  and  $\text{Y}_2\text{O}_3$  15 powders were dried at 500-700°C before mixing together and ball-milling in a zirconia container with zirconia balls. The mixture was fired at 1400°C for 10 hours.

The required amount of sintering aid was mixed together with as- 20 fired powder, ball-milled for 15 minutes twice, then pressed into pellets having a diameter of 13mm, before firing at 1300°C. Pure  $\text{ZnO}$  was used as the sintering aid and a dense  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  pellet was obtained. To minimise the effect of addition of  $\text{ZnO}$  25 on the other properties such as its conductivity, the amount of  $\text{ZnO}$  added was kept to a minimum. Less than 1wt% of  $\text{ZnO}$ , however, could not effectively sinter the  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  pellets.

With the addition of only 1w%  $\text{ZnO}$ ,  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  pellets may be sintered at a temperature as low as 1300°C. A relative density 30 of 96% was obtained after firing the  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  pellets at 1300°C for 10 hours with addition of 1wt%  $\text{ZnO}$ . For comparison,

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pellets pressed from 1400°C/10h BaZr<sub>0.8</sub>Y<sub>0.2</sub>O<sub>2.9</sub> powder without any ZnO, were also fired at 1300°C for 10 hours together with the pellets with 1wt% ZnO sintering aid. The latter were found to have a much lower relative density of only around 68% and 5 cracked into powders after exposure to air for just a few days.



